Chapter 11

Prediction of Blistering in Coating Systems

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Models based on diffusion and osmotic theory were developed for the growth of
water-filled blisters at the substrate beneath organic coatings. Blister growth was
considered to occur either over concentrated spots of impurity located at the point of
blister initiation, or over a surface containing a uniform distribution of impurity. The
solutions to both models had similar mathematical forms: the blister radius, surface
area, volume, osmotic pressure, all vary directly as fractional powers of time.
Experimental data for $KHSO_4$ as impurity was used to test the models. Blister
volume was found to vary as $t^{0.5}$ (vs. $t^{0.75}$ for the theory) and as M_s (vs. $M_s^{0.75}$),
where M_s is the mass of $KHSO_4$. Deviations between data and theory were discussed
in terms of the contact angle, blister initiation, ion concentrations within the blister,
saturation, disbondment, and possible mechanism shifts.

Organic coatings function by protecting substrates from physical and chemical attack.
In some instances, however, this attack can be promoted rather than hindered by the
presence of the coating. Such can be the case, for example when the substrate is
contaminated. Foreign ions, such as chloride or sulfate, present on the surface or
leached ions from the coating, can, in the presence of microscopic amounts of water,
establish local osmotic cells or blisters. Blisters also form and grow by other
mechanisms, for example, e.g.; swelling [1], phase separation during film formation
[2], temperature cycling [3], or loss of adhesion [4], but the osmotic mechanism for
growth is common [5].

Blister initiation does not occur when the surface is relatively clean, or where
water has not penetrated all the way to the substrate surface. Even with water present,
the osmotic pressure developed may be insufficient to destroy good adhesion between
the film and substrate. Blister initiation can also be prevented by reversing the
concentration gradient. Thus, if a concentrated salt solution is kept in the external
solution outside the coating, water may be drawn from the coating. This is the
principle which makes it possible to store acids and concentrated salts in well-painted
vessels made of metals, which would normally corrode. This helps prevent the
initiation of blisters and can collapse existing blisters.

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Both water and oxygen are capable of passing through the diffusion barrier provided by the organic coating [2, 5, 6]. The actual concentrations of corrosive agents present at the substrate-coating interface will depend on the permeability of the coating, which varies with temperature, partial pressure and the nature of the coating [6]. The film functions as a semi-permeable membrane allowing water to pass through but trapping ions present on the substrate surface within the blister [7]. The high pressures generated within the blisters can cause delamination of the film [7, 8, 9], and more water is osmotically driven into the blister. If oxygen is also present, then the potential for aqueous corrosion exists at the metal surface. Under most service conditions, there is sufficient time for the penetration of water and oxygen [10]. However for more severely corroding systems some evidence suggests that oxygen transfer rates through the coating may be rate limiting so that they determine the progress of corrosion reactions [2, 11]. Corrosion processes can release more ions, principally Fe^{++}, Fe^{+++}, and OH^-, and provide further blister enlargement by osmosis and cathodic delamination [12]. Blister growth due to corrosion is further complicated by precipitation of corrosion products within the blister (e.g., $Fe(OH)_3$, Fe_2O_3, and Fe_3O_4), and by concentration gradients established within the blister between anodic and cathodic regions.

Using time-series color photography and polarized light microscopy, in tests lasting from two to four days, Thomas [13] observed the initiation and growth of blisters beneath a transparent coating on a steel substrate. Small spots of inorganic salt $\left(KHSO_4\right)$ placed at the coating-steel interface were found to cause both blistering and corrosion. The corrosion that developed was localized within or near the blister. Cathodes developed near the periphery of the blister while anodes developed within the original spot of salt contamination. Corrosion products (hydrated iron oxides or rust) deposited between the anode and cathode. Results are consistent with the interpretation that anodic regions would tend to form at the center of the blister where oxygen concentrations are higher, while cathodic regions would form at the blister periphery where oxygen concentrations are lower [14]. At later times, blisters grew larger and anode "break-through" was observed. Cathodic blisters were also found to form external to the original salt contamination spot. The observations of Thomas are consistent with those of Leidheiser and Kendig [11] who studied the corrosion mechanism of polybutadiene - coated steel in aerated sodium chloride solutions.

In a series of papers, efforts towards an understanding of the mechanism for osmotic blister formation and growth were made by van der Meer-Lerk and Heertjes [7, 9, 15]. They studied the growth of small blisters under coatings of semi-permeable membranes with $KHSO_4$ salt deposited on the surface of the substrate. Their results indicated that water transport into the blister was not controlled by the mechanical resistance of the film to deformation [7]. This was demonstrated in an experimental study [9] in which water under pressure was used to artificially create blisters at the surface between different varnish films and substrates. Pressures needed to create blisters were substantially below these calculated to occur within osmotically generated blisters, an atmosphere or so, as compared to many atmospheres. The authors showed that water transport to the blister surface would not be controlled by disbonding or loss of adhesion (peeling) and stiffness. Adhesion loss was seen as a consequence of blister growth rather than a cause. van der Meer-Lerk and Heertjes proposed a mathematical model for the growth of blisters which was based on osmosis [15]. They considered water transport to be driven by the difference in chemical potential between the outside surface of the film and the inside of the blister. The initially high osmotic pressure developed within the blister decreased as it

became diluted with water. The size of the blister was assumed to increase at a rate proportional to the product of its curved (mantle) surface area, and the difference between the osmotic pressure $\Delta\pi$ and a compressive pressure P_k caused by the resistance of the film to deformation. Model results were compared to the data in terms of the product of the mean diffusion coefficient of water in the film $\overline{D}$ and mean concentration of water within the film $\overline{C}$, i.e., $\overline{DC}$, plotted as a function of the water activity coefficient within the blister (a_1). Results for different substrate-film pairs showed that $\overline{DC}$ increased only slowly with a_1 at low values of a_1 (less than 0.8), but rapidly for higher values, as the blister filled with water. A comparison was made between results for free films and attached films. Within experimental error it was found that substantially equivalent results were obtained. The authors took this as evidence that the overpressure P_k was negligible in comparison to the osmotic pressure $\Delta\pi$.

Blister Formation and Growth

This paper considers osmotically driven blister growth in the absence of corrosion. For corroding systems the results obtained can be considered to apply at early times, after blister initiation, when oxygen concentrations, and pH levels have not yet reached levels where corrosion is thermodynamically favored [16], or where it has not actually begun. Blistering is considered to initiate at the metal-substrate interface at weak spots randomly distributed over the substrate surface. These can be rough spots, spots with high impurity ion concentrations, or places with incipient adhesion loss. The weakest spots are ones where blisters will first initiate. Blister growth occurs when there is sufficient water present in the vicinity of the metal substrate. With time, the blisters may enlarge to a point where adjacent blisters coalesce. This can lead to complete detachment of the coating from the substrate. This paper is restricted to an examination of the growth of a single blister.

Foreign ions are presumed to be present already at the substrate-film interface as either a locally high spot of impurity or uniformly distributed over the surface of the substrate. Further, water transport to the blister is not limited by film adhesion or stiffness [9] and blisters grow solely by osmosis. The presence of salt contamination at the substrate surface causes a water activity difference between the outside and the interface. This difference induces an osmotic pressure potential causing water to flow from the outside towards the interface. When water has first penetrated to the substrate surface, it mixes with impurity ions present there and small liquid cells of locally high concentration form. Impurity anions, e.g., Cl^-, $SO_4^=$ and HSO_4^-, cannot diffuse out through the coating, which now acts as a semipermeable membrane. Alkali pigments can supply additional species to the ion pool within the blister, and cations, such as Na^+ and K^+ can be leached from glass, stone, or concrete substrates. As a result the osmotic pressure rises and more water diffuses into the cells, gradually enlarging them. In regions where the adhesion between the coating and the surface is poor, or where the concentration of impurity is especially high, the coating can disbond from the metal substrate and a blister can form. The blister continues to enlarge but at a slower rate as the solution is diluted and the osmotic pressure drops. The enlarging blister can also expose additional amounts of surface impurity ions.

Blister initiation and growth are coupled with the processes of adsorption, absorption, and diffusion of penetrants occurring within the organic coating. Absorption occurs by water update in the existing pores. Adsorption occurs by water uptake by the binding sites. Unlike absorption, it can be accompanied by heat release and swelling. Most water uptake in paints and polymers occurs by sorption. The interaction of sorption and diffusion processes depends on both time and distance scales. Thus, if blister initiation and growth is relatively slow compared to the time taken for water to diffuse to the interface, then blisters are more likely to form because of the proximity of water to the surface. The diffusion path for water will be much less than the thickness of the coating and diffusion times will be considerably shortened. If, on the other hand, blister growth is inherently faster than the diffusion rate of water, water will be drawn into the blister from the surface of the coating. The observed rate of blister growth will then be controlled by the uptake and diffusion rates of water. Diffusion of water through the film appears to occur relatively rapidly [5, 6, 10, 17], on a scale considerably faster than the growth of blisters. So although initial formation of blisters may be limited by the local availability of water, by the time blisters begin to grow, there is ample water in their vicinity. In addition, with only a few small blisters, there is minimal demand for more water.

In the models developed in this paper, impurity ions are considered to be either concentrated at specific spots on the surface where blister initiation occurs, or spread uniformly over the whole surface. Figure 1 depicts the two cases. With a uniform distribution of impurity, blister initiation still takes place over weak spots on the surface, but as the blister enlarges, new impurity ions are introduced at the periphery. In both models, it is presumed that adhesion loss and the stiffness of the organic coating do not control the rate of blister growth, so that the effect of the overpressure created by tension in the disbonding film can be neglected [15]. Thus, adhesion loss is considered to be an effect rather than a cause. At later times, the osmotic pressure may fall to the point that the adhesion in the film cannot be overcome. At this point blister growth will stop. It is also assumed that the coating itself contains no impurities that may migrate and change ion concentrations outside the film in the external solution or within the blister itself.

Analysis of Blister Growth

The analysis of the growth of a blister on a substrate beneath an organic coating is based upon a modified Fick's Law for diffusion which takes the flux of water N to be proportional to the product of the effective diffusivity $\overline{D}$ through the coating, the average concentration of water in the coating $\overline{C}$ and the gradient of the logarithm of the water activity coefficient (d ln a/dz) across the coating between the external environment and the interior of the blister [8]:

$$N = -\overline{DC} \; \frac{d \ln a}{dz} \tag{1}$$

Figure 1a depicts the profile of a single blister having the shape of a spherical segment. The contact angle is Θ, the base radius r, and h is the blister height. The contact angle (angle formed between the blister and the flat surface) is assumed to remain constant while both r and h increase as the blister enlarges [15]. The water activity coefficient in the external environment above the free surface is denoted by a_2 ($a_2 = 1$ for pure water). The distance z is measured normal to the coating from the surface. The blister is assumed to remain small relative to the coating thickness (h << L). This remains true for the initial and middle stages of blister growth. In later stages of growth, the blister may enlarge to the point where its size approaches or exceeds the
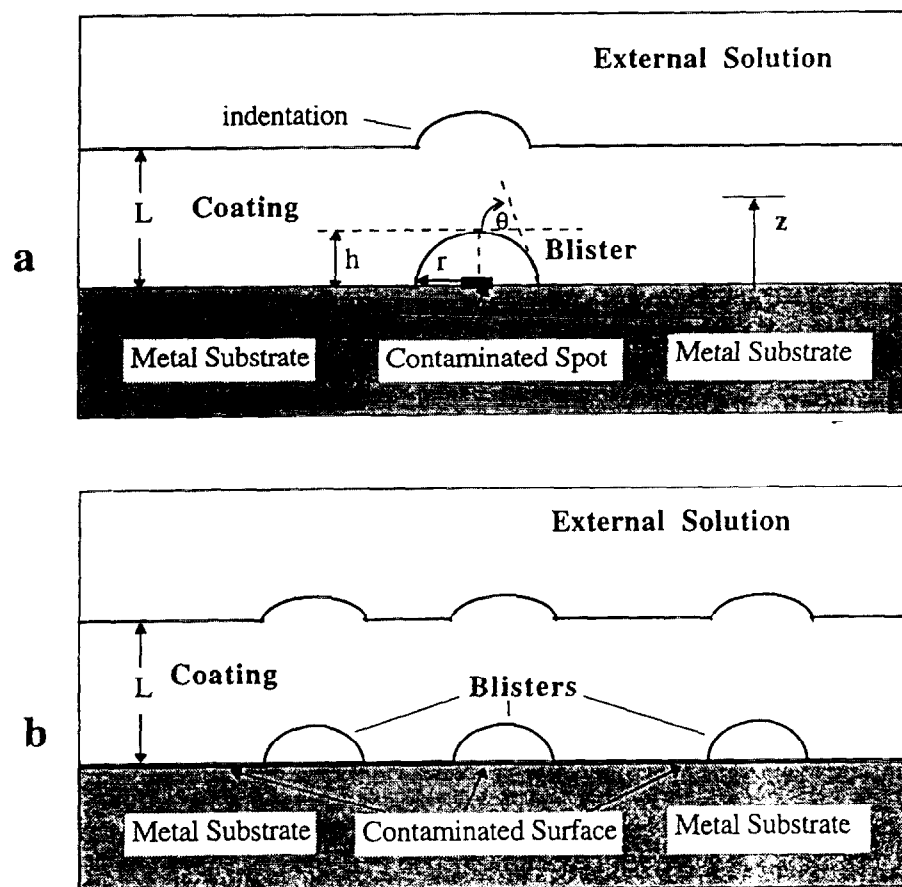
Figure 1. Schematic of blisters on coating surface
a: concentrated impurity, b: uniform distribution

initial film thickness L. In this event, the models presented in this paper may no longer apply.

It can be shown [18] that $d\ln a/dz$ is proportional to the concentration gradient of impurity ion, i.e., (dm/dz), where m is expressed as moles solute/liter solvent, so that:

$$N = \frac{\overline{DC\phi}}{\ell} \ \frac{\overline{M}}{1000} \ \upsilon \ \Delta m \tag{2}$$

where:

m	is the concentration of impurity ion
ℓ	is the diffusion path length
υ	is the number of ions formed from one molecule of impurity ion (valency)
$\overline{M}$	is the solvent molecular weight
$\overline{\phi}$	is the mean molar osmotic coefficient

The dimension ℓ represents a characteristic diffusion length. In cases where water must be drawn from the external environment, $\ell = L$, the coating thickness. When water is already present as a result of the molecular diffusion process then $\ell = \delta$, where δ represents a characteristic film thickness $(\delta \ll L)$ for the diffusion process. With little diffusional resistance, water in the vicinity of the blister would pass freely across the mantle surface and blister growth would be rapid. Equation (2) is based on constant values for D, C and ϕ. These can be considered as average or mean values over the film [15, 19], as denoted by the overbar. The multiplier of Δm on the right hand side of equation (2) is a constant which will be specific to the kind of impurity ion and coating involved. Δm represents the change in the concentration of the impurity ion between the blister and the outside of the coating. The diffusion process can be viewed as being driven by the osmotic pressure difference, $\Delta \pi$, which exists between the inside of the blister and the external environment. Thus:

$$\Delta \pi = \frac{RT}{\tilde{V}} \ \ell n \frac{a_2}{a_1} = \left(\frac{RT}{\tilde{V}} \frac{\upsilon \overline{M} \phi}{1000} \right) \Delta m \tag{3}$$

where:

R	is the gas constant
T	is the absolute temperature
$\tilde{V}$	is the partial molar volume of the solvent in the blister

For most salt solutions, it is reasonable to take $\tilde{V}$ constant and equal to C_i, the molarity of water. When no impurity ions are present in the external solution outside the coating, then $a_2 = 1$ and $\Delta m = m$. As the blister becomes diluted with water, a_1 rises, the osmotic pressure within the blister drops, and the diffusion process slows.

Concentrated Spots of Impurity. When dissolved impurity ions such as chloride or sulfate are present at a surface together with a sufficient amount of water, then blister initiation and growth occurs. Consider the surface to have a small spot where a high concentration of impurity ions are located, as shown schematically in Figure 1a.

A water balance equates the increase in mass of water within the blister to amount which fluxes through the mantle (curved) surface:

$$\rho \frac{dV}{dt} = \frac{dM}{dt} = \overline{M} \, S \, N$$ (

where:

- ρ is the density of water within the blister
- V is the volume of the blister
- M is the mass of water within the blister
- S is the mantle (curved) surface area

If the dissolution rate of hygroscopic impurity ions is high when compared the time scale for water diffusion, the dissolution is effectively complete before m\. water has had a chance to penetrate the blister and the concentration of impurity i within the blister can be expressed directly as:

$$m = \frac{1000}{M} N_s$$ (

Here N_s is the moles of salt contained within the blister. Taking the c where no impurity ions are present outside the film ($\Delta m = m$), and substitut equations (2) and (5) into equation (4):

$$\frac{dV}{dt} = \frac{N_s}{C_i^2} \frac{\overline{DC\phi}}{\ell} \upsilon \frac{S}{V}$$ (

This equation predicts blister growth rates that are directly proportional mantle surface area and inversely proportional to size. It applies to a blister of shape, e.g., spherical or ellipsoidal segments, such as were observed by van Meer-Lerk and Heertjes [7]. When the contact angle is not constant (most lik during the initial stages of growth), the theory developed here can be extended to co these cases. Equation (6) can be integrated numerically, if (θ, r), (θ, h), or (r, h) time data are available.

For blisters having the shape of the segment of a sphere (spherical ca equation (6) can be integrated to give the blister dimensions, surface area and volu as functions of time:

$$r = k_r \left[(1 + 1/2\cos\theta)^{-2}(1 - \cos\theta)^{-3} \right]^{1/4} \sin\theta \ t^{1/4}$$ (

$$h = k_r \left[(1 + 1/2\cos\theta)^{-2}(1 - \cos\theta) \right]^{1/4} t^{1/4}$$ (

$$S = 2\pi k_r^2 \left[(1 + 1/2\cos\theta)^{-2}(1 - \cos\theta)^{-1} \right]^{1/2} t^{1/2}$$ (

$$V = 2/3\pi k_r^3 \left[(1 + 1/2\cos\theta)^{-2}(1 - \cos\theta)^{-1} \right]^{1/4} t^{3/4}$$ (1(

where:

$$k_r = \left[\frac{6}{\pi}\frac{N_s}{C_i^2}\frac{\overline{DC\phi}}{\ell}\upsilon\right]^{1/4} \tag{11}$$

Details of the derivation of these equations are provided in the Appendix. As stated, the derivation is based on the assumption that the contact angle θ remains constant throughout blister growth [9]. For hemispherical blisters, where $\theta = \pi/2$, all of the angle dependent terms become unity and the equations simplify to previous results [8].

Equation (10) predicts that the blister volume increases as the 0.75 power of time. It also predicts that the rate of blister growth slows with time, being greater at the beginning when the blister is small and contains a concentrated salt solution, and less later when the solution in the blister has become diluted with water.

The osmotic pressure $\Delta\pi$ for concentrated spots of impurity is obtained by combining equations (3), (5) and (10):

$$\Delta\pi = \frac{3RT}{2}C_i^{3/2}\left[\frac{\upsilon\bar{\phi}}{\pi}(1+1/2\cos\theta)^2(1-\cos\theta)\right]^{1/4}\left(6\frac{\overline{DC}}{\ell}\right)^{-3/4}N_s^{1/4}t^{-3/4} \tag{12}$$

Equation (12) predicts that the osmotic pressure varies as the 0.25 power of the amount of salt in the blister and reciprocally with the 0.75 power of time.

Uniform Distribution of Impurity. The second type of blister growth model considers the impurity ion to be uniformly spread across the surface, as shown for several non-interacting blisters in Figure 1b. For the growth of a single blister, this differs from the previous model in one important aspect - as the blister grows, fresh impurity enters through its base. In this case the amount of impurity ion added to the blister N_s is proportional to the (flat) base area of the blister A:

$$N_s = k'A \tag{13}$$

The proportionality constant k' is equal to the surface concentration of impurity ions, mol/cm^2. For blisters having the shape of the segment of a sphere $A = \pi r^2$.

As in the previous development, it is presumed that the rate of dissolution of impurity ions into the blister is rapid compared to the rate of blister growth. Here, however, N_s will no longer be constant, since, as the blister peels from the surface, exposed impurity ions rapidly transfer into solution. By substituting equation (13) and equation (8) into equation (6), with $\Delta m = m$, it follows that:

$$\frac{dV}{dt} = k'\frac{\overline{DC\phi}}{\ell C_i^2}\upsilon\left(\frac{SA}{V}\right) \tag{14}$$

Equation (14) shows that for uniform distribution of impurity the blister growth rate is directly proportional to the mantle surface area, to the base area of the blister and inversely proportional to blister size. It applies to a blister of any shape. Using the expressions for r, S and V provided in the Appendix, equation (14) can be integrated to give the blister dimensions, areas, and volume as functions of time:

$$r = k'_r \left[(1 + \cos\theta)(1 - \cos\theta)^{-1/2}(1 + 1/2\cos\theta)^{-1} \right] t^{1/2} \tag{15}$$

$$h = k'_r \left[(1 + \cos\theta)^{1/2}(1 + 1/2\cos\theta)^{-1} \right] t^{1/2} \tag{16}$$

$$A = \pi k'_r{}^2 \left[(1 + \cos\theta)^2 (1 - \cos\theta)^{-1}(1 + 1/2\cos\theta)^{-2} \right] t \tag{17}$$

$$S = 2\pi k'_r{}^2 \left[(1 + \cos\theta)(1 - \cos\theta)^{-1}(1 + 1/2\cos\theta)^{-2} \right] t \tag{18}$$

$$V = 2/3\ \pi k'_r{}^3 \left[(1 + \cos\theta)^{3/2}(1 - \cos\theta)^{-1}(1 + 1/2\cos\theta)^{-2} \right] t^{3/2} \tag{19}$$

where:

$$k'_r = \frac{k'}{C_i^2} \frac{\overline{DC\phi}}{\ell} \upsilon \tag{20}$$

Again, these equations apply when the contact angle is constant, and reduce previously derived models for hemispherical blisters [8].

The osmotic pressure for a uniform distribution of impurity is given by:

$$\Delta\pi = \sqrt{\frac{3}{2}}\ RTC_i \left(\frac{k'\ell}{\overline{DC}}\upsilon \right)^{1/2} (1 + \cos\theta)^{1/2}\ t^{-1/2} \tag{21}$$

The osmotic pressure does not fall as rapidly in this case because of tl continual infusion of salt into the growing blister.

Results and Discussion

Figure 2 presents a logarithmic plot of blister volume V $\left(\text{in } \mu m^3 \right)$ vs. exposure tin (in days). Data were taken from the paper of van der Meer-Lerk and Heertjes [7] fi concentrated spots of $KHSO_4$ having three different initial masses. According equation (10) the lines should have a slope of 0.75. However a slope of 0.5 fits mo of the data well. Since the blister volume can be expressed as $V = k_v t^n$, whe: $n = 1/2$, the value of k_v, the volumetric growth constant, is found from the interce of each of the lines in Figure 2. Figure 3 shows a log plot of k_v vs. the mass KHSO$_4$, M_s. The slope of this plot is 1.1 indicating that k_v is nearly proportional ı the mass (or moles, N_s) of salt contained within the blister. The model for concentrated spot of impurity predicts that $k_v \sim N_s^{3/4}$. Thus, theory predicts th; $V \sim N_s^{3/4} t^{3/4}$, whereas the experiments give $V \sim N_s t^{1/2}$. So for a fixed amount c salt, blisters grow at a slower rate than predicted, but at any fixed time using more sa results in higher rates of blister growth than is predicted by theory. Blister growth i generally slow enough that it is not limited by the availability of water. However, ; longer times lower growth rates would result if the osmotic pressure fell to the poir where it approached the disbonding pressure. Lower growth rates would then be th result of increasing film stiffness as the film resisted further disbondment. On th
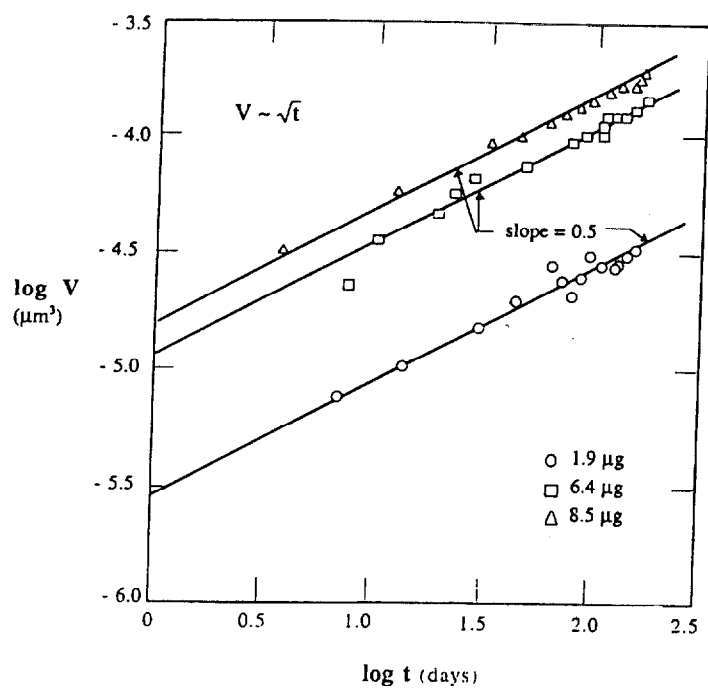
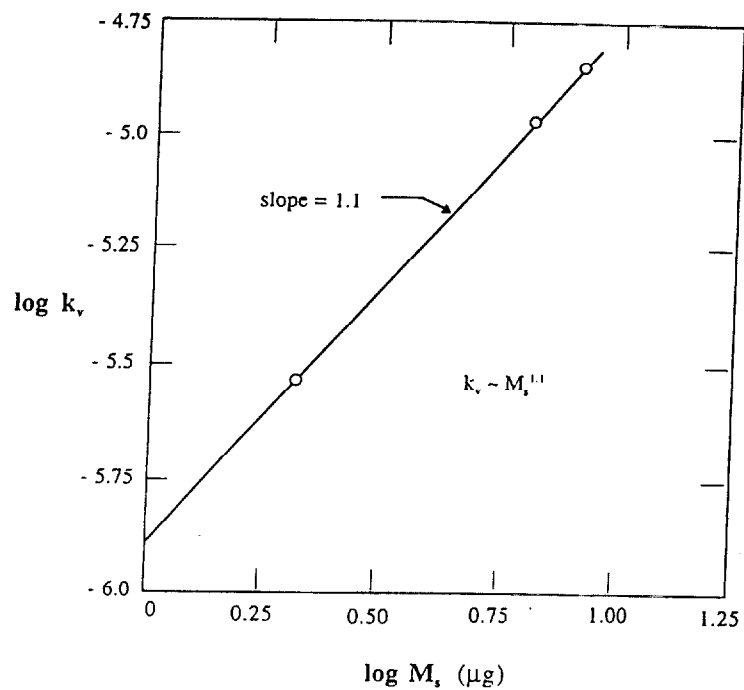Figure 2. Blister volume (μm^3) vs. time (days)
[logarithmic plot]

Figure 3. Volumetric growth constant (k_v) vs.
mass of impurity (μg) [logarithmic]

other hand, higher blister growth rates may be due to the gradual leaching of w soluble species to the interface as reported by Walker [20]. Then the concentration ions in the blisters would be higher, which would drive water faster from the out to the interface.

Although the exponents are not precisely equal to the theoretical values, tl results show that dimensions and rate constants for blister growth can be expresse simple power law functions of exposure time. Lower growth rates are expected if blister initially grew very rapidly to the size of the salt patch, or if the concentra within the blister remained constant at the start until all the $KHSO_4$ had dissol With $m = m*$, the saturation concentration, the volumetric growth rate dV/dt w vary directly as t^2 rather than t until m fell below $m*$. At that point (time t_0, with l radius r_0) growth rates would slow and blister size could be predicted by integra equation (A - 5), with $r = r_0$ at $t = t_0$. This procedure would handle any case w! the initial blister size was not zero, or where such a mechanism shift occurred.

In many cases, the salt spot on the surface is present as a small patch or r With the availability of water, surface diffusion gives a more or less uniform content over the patch. (It is likely that the center of such a spot has a slightly hi salt concentration so that blister initiation is favorable there.) The model develope uniform salt distribution is applicable until the blister has grown to the size of patch, after which the model for concentrated salt distribution applies. At this time blister growth rate would abruptly decrease. The experimental data [7, 15] do show a break in slope, but data were not collected at early times where su mechanism would be most likely. Both models have the same mathematical form radius, surface area and blister volume all vary directly as the time raised to van fractional powers. Comparing model solutions for concentrated impurity distribu with those found for uniform salt distribution predicts that the blister size incre more rapidly with a uniform salt distribution.

For both models, the osmotic pressure is predicted to fall with time as solution within the blister becomes diluted with water. The models predict an ini osmotic pressure at time zero. In actuality, the highest osmotic pressure would be corresponding to the saturation value of the impurity salt in water. The osn pressure drops most rapidly when the salt is initially concentrated within the b rather than being uniformly spread across the substrate. When all the sa concentrated within the blister, the initial osmotic pressure is much greater than v the salt is uniformly distributed. For uniform salt distributions, osmotic pressu not predicted to fall as fast because fresh salt is being added at the periphery o blister. It is best to compare osmotic pressures based on the availability of the total amount of salt to the blister.

The results of this study can be extended to consider the growth of a fie blisters and to situations where blister formation and growth is coupled with corr reactions.

Nomenclature

a_1	water activity coefficient within blister
a_2	water activity coefficient in external solution
A	flat area of blister on metal surface
$\overline{C}$	mean concentration of water within coating
C_i	concentration of water within blister
D	diffusion coefficient or diffusivity of water in coating
$\overline{D}$	mean value of D

h	height of blister
k_r	rate constant for blister radius growth
k_v	volumetric growth rate constant for blister volume
k'	surface concentration of impurity ions, based on area
ℓ	effective diffusion path length
L	thickness of coating or film
m	concentration of impurity ion
m^*	saturation value of m
M	mass of water in the blister
M_s	mass of salt present within blister
$\overline{M}$	solvent molecular weight
$\overline{M}_s$	salt molecular weight
N	diffusive flux
N_s	moles of salt present within blister
P_k	film pressure
r	radius of base of blister
R	gas constant
S	surface area of blister mantle
t	time
T	absolute temperature
V	volume of blister
$\tilde{V}$	solvent partial molar volume
z	depth into coating measured from coating-substrate interface

Greek Letters

$\Delta\pi$	osmotic pressure within blister
υ	number of ions formed from one molecule of impurity ion (valency)
ϕ, $\overline{\phi}$	molar osmotic coefficient, mean value
ρ	density of water within blister
θ	contact angle

Appendix

Consider a blister having the shape of the segment of a sphere or spherical cap as depicted in Figure 1a. The contact angle, blister height and radius of the base are related by:

$$\frac{h}{r} = \tan(\theta/2) = \frac{1 - \cos\theta}{\sin\theta} \tag{A-1}$$

Equation (A-1) shows that, if the contact angle remains constant during blister growth, there is a simple proportionality between h and r. van der Meer-Lerk and Heertjes [9, 15] found that the contact angle was constant, except at the beginning of their experiments.

The blister volume and mantle surface area S are given by:

$$V = \frac{\pi h^3}{6}\left[1 + 3\left(\frac{r}{h}\right)^2\right] \tag{A-2}$$

$$S = \pi h^2\left[1 + 3\left(\frac{r}{h}\right)^2\right] = \frac{2\pi rh}{\sin\theta} = \frac{2\pi r^2}{1 + \cos\theta} \tag{A-3}$$

Combining equations (A-1) and (A-2):

$$V = \frac{2}{3}\pi r^3 \frac{\left[1 - 3/2\cos\theta + 1/2\cos^3\theta\right]}{\sin^3\theta} \tag{A-4}$$

Equation (A-4) has been used to calculate contact angles for small droplets based on experimental measurements of V and r [21].

For concentrated spots of impurity, equation (6) is used. dV/dt is found in terms of r by differentiating equation (A-4), with the contact angle held constant, while S/V is expressed as a function of r using equations (A-3) and (A-4). This leads to:

$$r^3\frac{dr}{dt} = \frac{3}{2\pi}\frac{N_i}{C_i^2}\frac{\overline{DC\phi}}{\ell}\upsilon\frac{\sin^6\theta}{\left(1 - 3/2\cos\theta + 1/2\cos^3\theta\right)^2}\frac{1}{1+\cos\theta} \tag{A-5}$$

Integration of equation (A-5) with $r = r_0 = 0$ at $t = 0$, leads to equation (7). Expressions for h, S and V (equations 8, 9 and 10) follow directly by substituting equation (7) into equations (A-1), (A-3) and (A-4), respectively.

For uniform distribution of impurity, equation (14) is used. As before dV/dt and S/V are expressed as functions of r, while $A = \pi r^2$. With the assumption that the contact angle remains constant, this leads to:

$$r\frac{dr}{dt} = \frac{3}{2}\frac{k'}{C_i^2\overline{M_s}}\frac{\overline{DC\phi}}{\ell}\upsilon\frac{\sin^6\theta}{(1+\cos\theta)\left(1 - 3/2\cos\theta + 1/2\cos^3\theta\right)^2} \tag{A-6}$$

Integration of equation (A-6) with $r = r_0 = 0$ at $t = 0$, leads to equation (15). Expressions for h, A, S and V follow directly.

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